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Evaluation of several ultra- and nanofiltration membranes for sugar control in winemaking

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Abstract

Several membranes are here considered and studied in order to be applied to control of the sugar content of grape musts. This should allow decreasing somewhat the alcohol degree of wines that due to a warmer weather are being made from too mature grapes sometimes. This gives wines with a too high alcohol degree. Our objective is to reverse this degree to the original one without loosing the main appreciated characteristics of these wines.

A non-aggressive technology that can be used in such a procedure consists in membrane processes. Total sugar retention and specifically glucose and fructose rejection have been studied both in must and synthetic water solutions through nanofiltration and tight ultrafiltration membranes. Also the most relevant high molecular weight (HMW) compounds of must along with their low molecular weight ones (LMW) have also been analyzed. From a detailed consideration of these retentions as a function of sugars that allow to design an adequate two steps nanofiltration process.

Keywords: Winemaking; Must; Alcohol reduction; Sugar retention; Nanofiltration

1. Introduction

Due to the climate change, previous years have been warmer and dryer in some regions. As a consequence of that, an early ripening of grapes takes place which increases sugar content. Thus, fermentation should lead to alcoholic degrees higher than desired. An adequate control of sugars in musts can also be useful to obtain low alcohol degree wines which are demanded by certain markets. As a consequence, it should be useful to have technologies that could correct this tendency to get too high alcohol degrees. One of these mild and highly specific technologies required

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involves the use of membrane processes. These technologies have the advantage of avoiding any addition of limited or forbidden products. On the other hand, the high sugar containing by-products could be used to manufacture liquors or as additives to other food processes.

Concentrated must is a natural sweetener in wine production and a vitaminated and aromatic drink. To obtain such concentrates is the aim of some applications of membrane processes to treat musts [1]. In this work, Kiss et al. regulated the resulting sugar content to allow the preservation of the resulting must and they conclude that nanofiltration is a process alternative to conventional evaporation attending to economical considerations.

Nanofiltration has also been used to increase the sugar content of grape must used for wine production [2]. Versari et al. [2] obtained relatively high sugar retentions (7–97%) with low retention of malic acid extent (ranging from 2% to 14%). A two-stage NF process of grape must removes a small volume of permeate and concentrates sugars to a potential alcohol degree near to 16% with a high content of polyphenols. The direct filtration of wines, usually alters its organoleptic characteristics. Nevertheless red wine contains many compounds which have a beneficial effect on human health this is why Banvolgyi et al., [3], have nanofiltered red wine to concentrate such valuable components of red wine.

Attending to the molecular weight of sugars in must, nanofiltration should be the membrane process to be chosen with such an aim. Here we analyze several membranes and their retentions for glucose and fructose in synthetic mixtures and also along with other relevant components in a commercial must.

2. Experimental

The main nominal properties of the selected membranes are shown in Table 1. They are UF-GH, NF-HL, and NF-DK and are made and commercialized by GE Water & Process Technologies. The water permeabilities of these membranes have been measured.

Table 1
Nominal characteristics of the membranes used

	Membrane		
	UF-GH	NF-HL	NF-DK
Cut-off retention	1 kDa for PEG	98% for $MgSO_4$	98% for $MgSO_4$
Water permeability (10^{-11} m/Pa s)	0.89	2.67	1.51

Permeation and retention have been measured by using a tangential flow module with a single channel of 110 mm × 60 mm × 0.5 mm described elsewhere [4]. The applied pressures ranged from 5 to 20 bar and the recirculation velocity from 1.7 to 3.3 m/s.

Firstly, isomolecular mixtures of glucose and fructose at a total concentration of 249.58 g/L (which is usually encountered in musts) have been filtered though the selected membranes. The observed retentions were measured too. In these experiments, concentrations were measured by differential refractrometry.

A commercial must containing slightly unbalanced sugars (44.4% glucose – Gl and a 55.6% fructose – Fr) has been also filtered and the resulting retentions for polyphenols, anthocyanins, tartaric acid and potassium have been measured. In this case, fouling was relevant thus the volume flow decay was studied too at high applied pressures from 10 to 20 bar.

Total sugars were evaluated by absolute refractometry and polarimetry; glucose, fructose, tartaric acid and potassium were analyzed according to the OIV methods [5]. Polyphenols were determined by reaction with Folin–Ciocalteu reagent and were expressed as mg/L of gallic acid [6]. Anthocyanins were quantified according to colour variation in function of pH, and were expressed as mg/L of malvidin-3-glucoside [6].

Table 2
Water permeabilities

	Membrane		
	UF-GH	NF-HL	NF-DK
L_p (10^{-11} m/Pa s)	1.36	7.67	3.11

3. Results

The water permeabilities before the filtrations are shown in Table 2. Note that the permeabilities given here are substantially higher than those given by the manufacturer probably because those have been measured through a spiral wound module while now we have measured them for a flat single membrane. There is no significant reduction in the water permeability after the filtration of the isomolecular mixture of sugars, which confirm that in this case fouling was irrelevant. In the case of must, comparatively there is an important decay of flux as shown in Fig. 1.

The observed retentions for the isomolecular glucose–fructose solution along with those for the commercial must are shown in Fig. 2. Glucose and fructose are equally retained specially for high sugar retentions. Obviously, the observed retention is lower for sugar in water than in must. This is due to the interaction with the other relevant compounds in the grape unfermented must.

Observed retention is shown as a function of the applied pressure in Fig. 3. The observed retention for polyphenols, anthocyanins, tartaric acid and potassium are also shown, as a function of those for total sugars in must, in Fig. 4. Where it is seen that there is a tendency of increasing

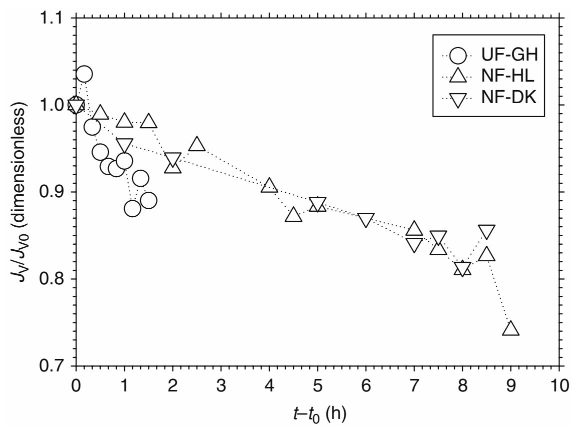

Fig. 1. Normalized volume flux versus time after first flux detected. Applied pressure were 10 bar for the GH membrane and 20 bar for the other two.

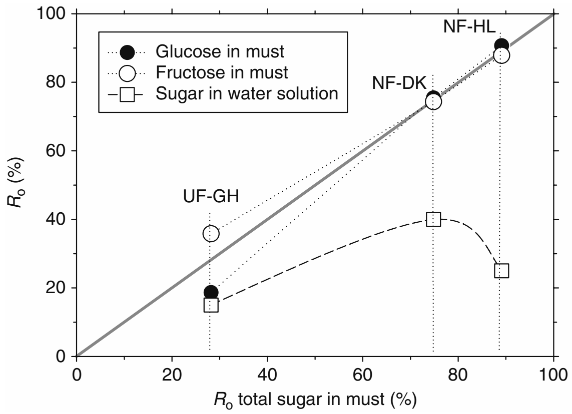

Fig. 2. Observed retention for glucose and fructose in must and total sugars in the isomolecular water solution as a function of the total sugar retention in must. These retentions appear at an applied transmembrane pressure of 10 bar for the GH membrane and 20 bar for the other two.

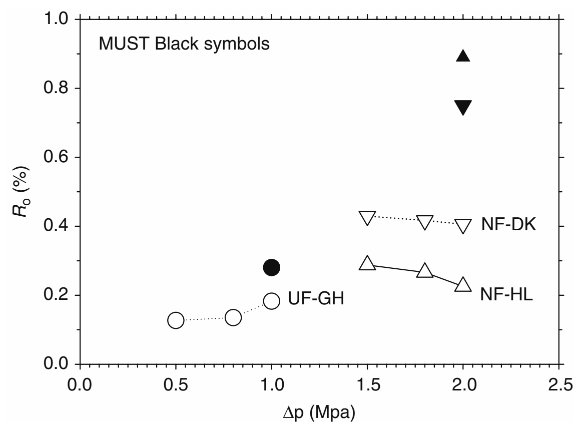

Fig. 3. Observed retention of total sugars as a function of applied pressure.

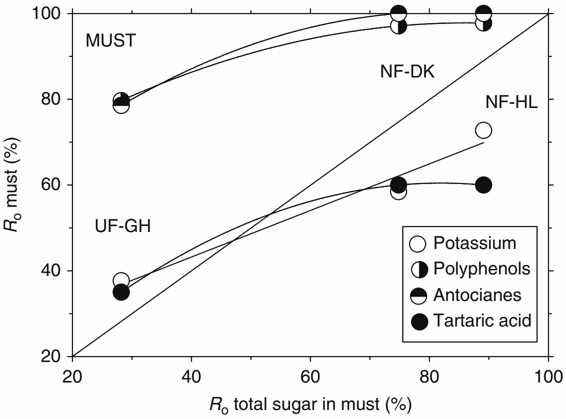

Fig. 4. Observed retention for some HMW and LMW relevant components of must as a function of those for total sugars in must. These retentions appear at an applied transmembrane pressure of 10 bar for the GH membrane and 20 bar for the other two.

retentions for all the relevant components of must with the retention of total sugar is observed. These components should be preserved as far as possible in order to keep pH, colour, structure and body of the final wine.

Note that in order to have a significant reduction in sugars, the nanofiltration DK and HL membranes could be used. Within them the HL membrane doubles more than the permeability of DK. Besides this membrane retain only low amounts of potassium and tartaric acid. Both these components determine the acidity and pH in wine after fermentation, that we would not like to change substantially.

On the other hand, both these membranes retain almost all polyphenols and anthocyanins which determine the colour of the resulting wine. Thus, a procedure of reconstitution of the must before fermentation should be tried. One of such procedures is outlined in Fig. 5. In a procedure like this, two successive nanofiltration steps should be included, the permeate of the first step should contain moderate amounts of sugar and practically no high molecular weight compounds (namely polyphenols and anthocyanins), HMW. Then if the second step is run until the retentate reaches a too high viscosity, the corresponding permeate should contain very low amounts of

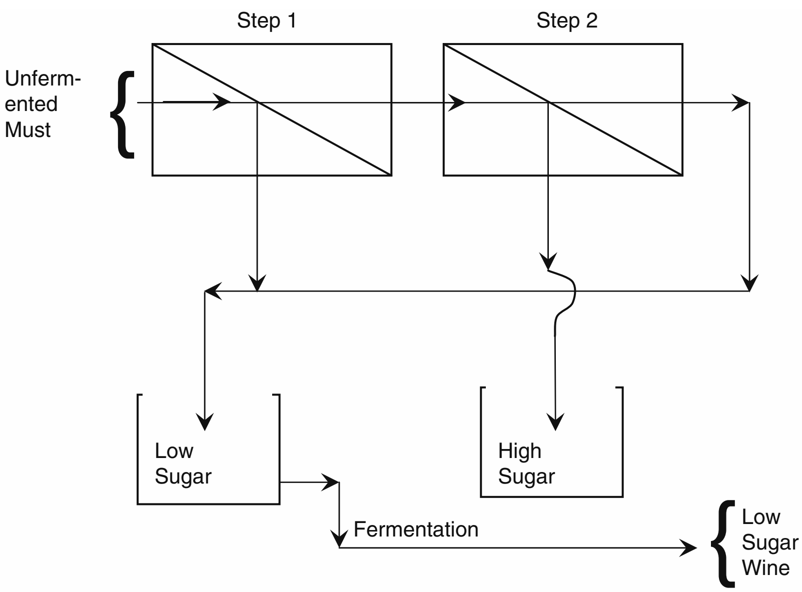

Fig. 5. Tentative scheme of a two-stage membrane process allowing a reconstitution of the must to include both LMW and HMW components.

sugar and almost all the low molecular weight compounds (ions and tartaric acid among others), LMW. Then a mixing of these two streams should give a must with almost all LMW and HMW compounds with a content of sugar below the original must. While the very small residual volume remaining from the retentate of the second step has a high percentage of sugar and can be used to other purposes.

If the first step was substituted by an ultrafiltration process the HMW compounds should be lost with the high sugar stream. And finally if the second step was substituted by a RO process, the components that should be lost with the high sugar stream should be the LMW components of must.

4. Conclusions

Several membranes have been evaluated with the aim of allowing the control of sugar in grape musts. The final objective is to decrease slightly the alcohol content of wines manufactured from over riped grapes to keep the alcohol degree within the traditional ranges accepted by the consumer without altering the specific organoleptic balance of the resulting wines.

After a detailed consideration of the retention characteristics of the membranes studied, a two-step nanofiltration process is proposed with a remixing of the first retentate with the second permeate that should have a composition very similar to the original must both in LMW and HMW compounds with lower concentration of sugars. The fermentation of this mixed must should decrease slightly the alcohol degree with no concomitant changes in the wine personality.

Among the membranes studied by us NF-HL seems to be the adequate one as far as gives a relatively low or moderate retention of LMW compounds with a very high permeability, thus decreasing the energy income required.

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